Chapter 10

Selection of surrogates for jet fuels

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Abstract: A detailed characterization of JP fuels is provided based on literature data for the average of 55 worldwide and 4 US Jet-A fuels. These are complemented by NMR analysis of a JP-8 that provides the fractions of the carbon in the fuel that are present as protonated, bridgehead, and non-substituted aromatic carbons and the fractions of aliphatic carbons present methyl, methylene, methine, and quaternary structures. A JP-8 fuel for the study was proposed that satisfied the Jet-A average composition as well as the NMR data. The composite results were used to obtain model representations of chemical compositions of a JP-8 that satisfied the constraints imposed by the classes of chemicals, carbon chain lengths, and average number of substituents for the US average and the breakdown of carbons determined by NMR experiments. The results provide a complete characterization of the n-paraffins, iso-paraffins, cyclo-paraffins, benzenes, tetralins, indans, and napthalenes. The model representations have been used to show how the class distribution of compounds and the side chain substituents on both aromatic and aliphatic fractions influence soot formation.

1. INTRODUCTION

Surrogate formulations are now commonly used to represent practical fuels in computer simulations and to provide reference fuels for use in characterizing the combustion behavior of fuels without the variations inherent in the composition of real fuels because of differences in crude source, refinery conditions, and aging. Furthermore, the complexity of real fuels makes it impossible to follow, in detail, the physical and chemical processes involved in combustion. Surrogate formulations in current use vary widely depending upon the properties, physical or chemical, of the real fuel that needs to be reproduced. The present paper describes the characterization of jet fuels and the development of methods for defining surrogates for selected applications. In this study, we will complement the excellent review on surrogate jet fuels provided by Colket et al. [1], providing additional information on the use of NMR for functional group analysis and on selecting surrogates that accurately match the sooting characteristics of jet fuels.

1.1. Origin of jet fuels

Jet fuels are derived from crude petroleum as a distillate cut of about 140 to 300 C, as shown schematically in Figure 1 (adapted from Speight [2]). This figure also provides

the distillate ranges for other common transportation fuels for comparison. The components of petroleum are determined by its biogenic origin, modified by the molecular scrambling that occurs during geological time spans. From Figure 1 it can be seen that the major classes of compounds contained in petroleum are normal and branched (iso-) paraffins, mono- and polycyclic cycloparaffins (also known as cycloalkanes and naphthenes) and mono- and polynuclear aromatics. Within the distillate cut for jet fuels it can be seen that the relative amounts of the different classes change with boiling temperature with the concentrations of polycyclic paraffins and polynuclear aromatics increase with boiling point while the total paraffin content decreases. The aromatic and polycyclic paraffins are usually substituted, several substituents per ring. The iso-paraffins often reflect their biogenic origin, i.e., they have structures clearly derived from those of saturated polyisopranes (methyl substituted n-paraffins with three methylene groups between successive methyl substituents). The composition of jet fuel will vary with the composition of the parent crude, the refining conditions, and small amounts of additives used (e.g., U.S. domestic airlines often use Jet-A fuels with a higher freezing point, called Jet-A1, to reduce cost; JP-8 will typically include a military additive package; see page 29 of reference [3] from Chevron). An important measure of the variability in sooting tendency of jet fuels is the aromatic content, which ranges from

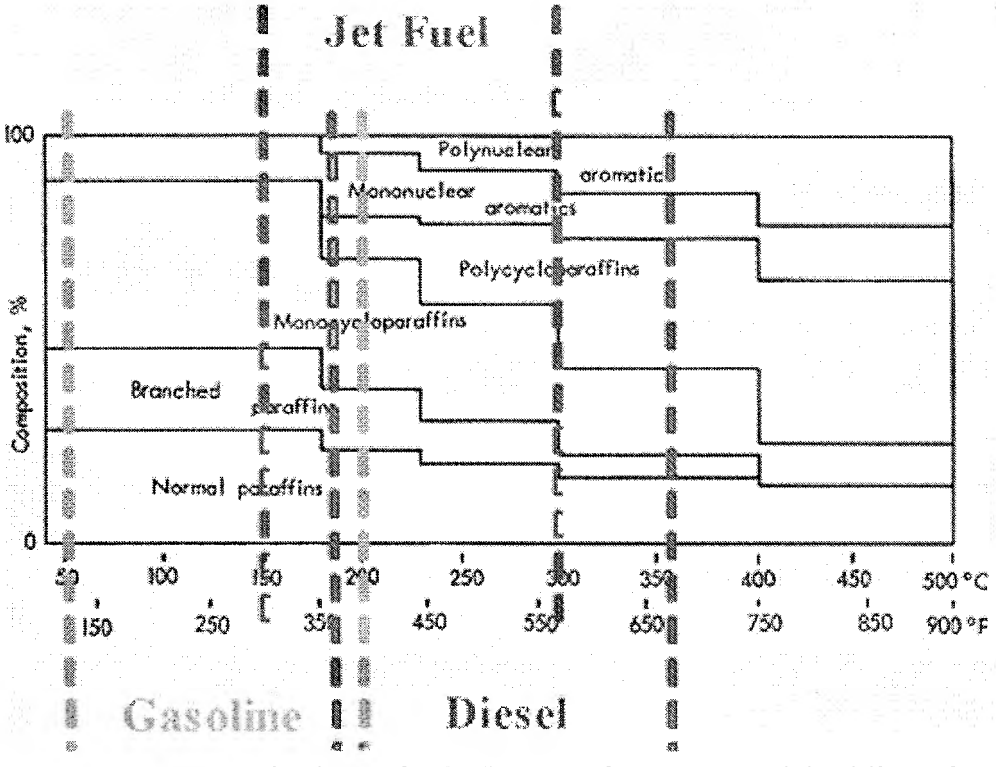


Figure 1. Composition distribution for distillate cuts of petroleum used for different fuels (adapted from Speight [2]).

11.5 to 25% by volume in JP-8 deliveries during 2004 (see Figure 1 in Colket et al. [1]). Additional measures of variability are provided by the percentage range of chemical classes in jet fuels from four US refiners specified by Edwards [4] for aviation fuels. The aromatic content ranges from 8% to 26% by volume with a mean of 19.1% (σ = 3.1%). Monocyclic paraffin content ranges from 0 to 26% (estimated mean 13.4%, σ = 4.8%) and iso- plus normal paraffin content ranges from 34 to 78% (mean 55.1%, σ = 7.6%, with 17.6% normal paraffin).

1.2. Characterization of fuels

Jet fuels are composed of thousands of compounds, present in widely varying amounts that fall into the classes shown in Figure 1. A gas chromatographic (GC/MS) analysis of a Jet-A fuel is shown in Figure 2. The peaks for normal paraffins, present in relatively high concentrations, stand out clearly (the odd ones only are marked) but many (in the thousands) peaks represent compounds in low concentration and form an unresolved hump that can only be analyzed by additional fractionation to separate

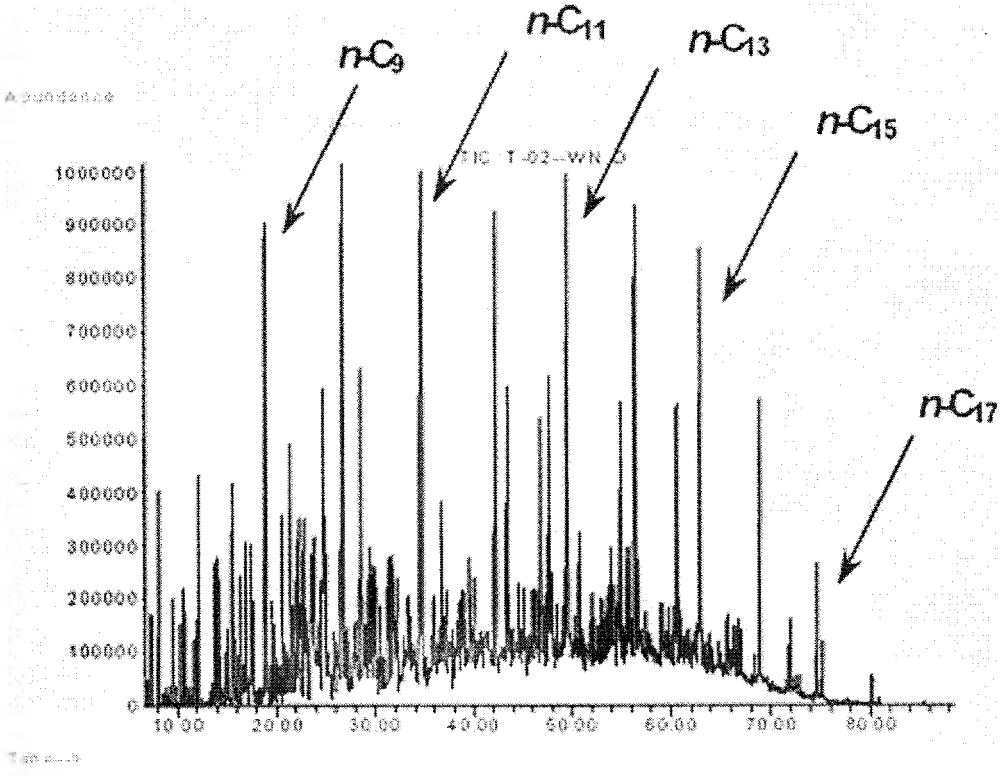


Figure 2. Gas chromatogram of a Jet-A fuel with prominent peaks labeled for n-paraffins having an odd number of carbons.

the compounds. As a first approximation, the boiling point of a compound increases by about 20 C per carbon number, but the boiling point varies with compound class for molecules of the same carbon number being, for example, higher for more compact molecules (smaller specific molar volumes) such as aromatic compounds. Note that the normal paraffins identified here run from C_9 to C_{17}, consistent with a boiling point range of 160 C. The boiling point range determines the range of carbon numbers in the different classes. For a typical jet fuel, the average carbon number may vary from 9 to 16 for paraffins (normal and iso-), 8 to 15 for cyclo-paraffins, and 7 to 14 for aromatics.

2. CHEMICAL CHARACTERIZATION OF A TYPICAL JP FUEL

The average composition, by chemical class, reported [1], for 55 international (world) jet fuels are summarized in column 1, 4 US jet fuels [9] in column 2, and a specific JP8 fuel selected for the present study in column 3 of Table 1. The rows provide the average volume percent of the different chemical classes for each fuel category. The cycloparaffins are further subdivided into mono-, di-, and tri-cyclo; the substituted benzenes are classified under benzenes; the tetralins, indans and napthalenes also include substituted compounds. The compositions for the JP-8 are also reported on a mole percent and a weight percent basis in columns 4 and 5. The conversions from volume to mole and weight percent were made using average properties for each class of hydrocarbons. Average carbon numbers are listed in column 6 for each class, based on the measurements by Hodgson and Kremmer [10] for a Jet-A fuel; average densities (column 7) and molecular weights (column 8) of each chemical class were calculated using several representative compounds for each class of compounds as shown in the footnotes to Table 1.

The data in Table 1 are average numbers over the boiling point distribution. From the range of boiling points in Figure 1, as mentioned previously, one can expect a variation in the composition of the different distillate cuts of the JP fuels, with the lower boiling point compounds having carbon numbers typically between 7 and 9, composed of lighter paraffins and monocyclic aromatics and cycloparaffins. The higher boiling point compounds will typically have carbon numbers of 14 to 16 with significant concentrations of bicyclic aromatics and cycloparaffins and lower concentrations of tricyclic compounds. Complementary information on the composition of JP fuels is provided by NMR data.

2.1. NMR analysis of jet fuels

NMR spectroscopy, in conjunction with other spectrometric information, has been used extensively in identifying organic compounds. The present account is intended to be sufficient for our limited objective, i.e., to differentiate the structural features in jet fuels at the sub-molecular level. NMR spectroscopy is extremely sensitive to the nature of the bonds connecting the atoms of a molecule as well as the molecular dynamics of the structure. Each atom has a unique chemical signature called a chemical shift

Table 1. The composition of world average, US average, and JP8 used in this study.

Species class	world avg vol %	US avg vol %	JP-8 fuel vol %	mol %	Weight %	Avg C No.	Density (g/ml)	Mol weight
n-paraffins	18	17.6	20.6	18.12	16.34	12	0.749[a]	170.3[a]
iso-paraffins	41	37.5	37.9	35.05	27.35	12	0.759[b]	164.3[b]
cyclo-paraffins	21.1	25.8	26.05			12		
mono-cyclo	11	13.45	13.65	14.37	13.49		0.81[c]	154[c]
di-cyclo	9	11.0	11.1	11.78	12.00		0.88[d]	166[d]
tri-cyclo	1.1	1.35	1.3	1.28	1.61		0.944[e]	192.3[e]
benzenes	13.3	12.8	9.4	11.50	13.99	10.7	0.88[f]	144[f]
tetralins/indans	5	4.8	5.05	6.58	5.69	11	0.958[g]	146[g]
naphthalenes	1.6	1.5	1	1.34	1.86	11.5	1[h]	149[h]
Total	100	100	100	100	100		0.803[i]	

[a] The average normal paraffin is C_{12} [4]; therefore the physical properties of normal paraffins were assumed to be the averages of normal undecane, dodecane, and tridecane. All density data were obtained from the CRC handbook [5].

[b] Represented by the narrow distillate cut of Isopar H, the analytical composition of which indicates 38% C_{11} and 60% C_{12} species, with an average of 3.25 branches [6], equivalent to an average chemical formula of $C_{11.6}H_{25.2}$. Density of Isopar H was obtained from ExxonMobil [7].

[c] Assume the average chemical formula for monocyclo-paraffins to be $C_{11}H_{22}$ [1, 4]. Pentyl cyclohexane was used for the average density as the reference species.

[d] Assume the average chemical formula for dicyclo-paraffins to be $C_{12}H_{22}$ [1, 4]. Density was taken to be the average of cis and trans decalins.

[e] Reference species is tetradecahydro phenanthrene.

[f] Assume the average chemical formula of alkylated benzenes to be $C_{10.7}H_{15.4}$ [4]. Tert-butyl methyl benzene and 2-ethyl cumene were used as reference species for the average density.

[g] Assume the average chemical formula of tetralins/indans to be $C_{11}H_{14}$ [4]. Methyl and dimethyl tetralins and indans were used as reference species for the average density.

[h] Assume the average chemical formula of naphthalenes to be $C_{11.5}H_{11}$ [4]. Reference species are methyl and 1- and 2- ethyl naphthalenes.

[i] Calculated using the volume % of the JP8 fuel. The reported range of densities for JP8 at 15 C is between 0.775 and 0.840 g/ml [4, 8].

relative to a standard reference compound. For hydrocarbon fuels, the carbon-13 chemical shifts can be used to identify the classes of compounds discussed above.

NMR spectra used for this study were recorded on a Varian Inova 500 spectrometer operating at 125.64MHz for ^{13}C. Deuterated Chloroform ($CDCl_3$) was the solvent, and tetramethylsilane (TMS) was added to provide a chemical shift reference. Broadband proton decoupling was used in all cases.

Although the principles are quite well understood, prediction of chemical shits from molecular structure is quite complex. For alkanes, both normal and iso-, chemical shifts can be predicted quite accurately using simple additivity rules explained in many elementary NMR texts. (See, for example, reference [11].) Chemical shifts depend most strongly on neighboring atoms one or two bonds removed from the

atom in question but are influenced to a lesser extent by neighbors connected through three or more bonds. Orbital hybridization and electronegativity of substituents are prime factors in determining chemical shift, but steric crowding, solvent, concentration, and temperature may also be important. In the case of hydrocarbon fuels, the "solvent" may consist mainly of the other thousands of compounds in the fuel; and, thus, natural variations in the composition of samples of the same fuel type from different sources may slightly alter the chemical shifts of a given component.

Probably the most accurate way to predict the chemical shifts of an unknown compound is to compare its chemical shifts to a library of known compounds. Spectra of hundreds of thousands of compounds have been catalogued and computer programs have been devised to predict structure from a list of chemical shifts or to predict chemical shifts of a given structure.

In Figure 3, the chemical shifts of the aliphatic carbon atoms in the various components of a surrogate fuel, Hex12, are given. Primary carbons (methyl groups, CH_3) in normal paraffins appear upfield at 14.2 ppm on the standard reference scale. The C2 and C3 carbons (CH_2, methylene) show a progressive deshielding (downfield) trend. Of course, for a chain of length n, Cm carbons have the same chemical shift as Cn-m+1 carbons, i.e., carbons at the same distance from the ends of the normal hydrocarbon chain exhibit identical chemical shifts, since they experience identical bonding

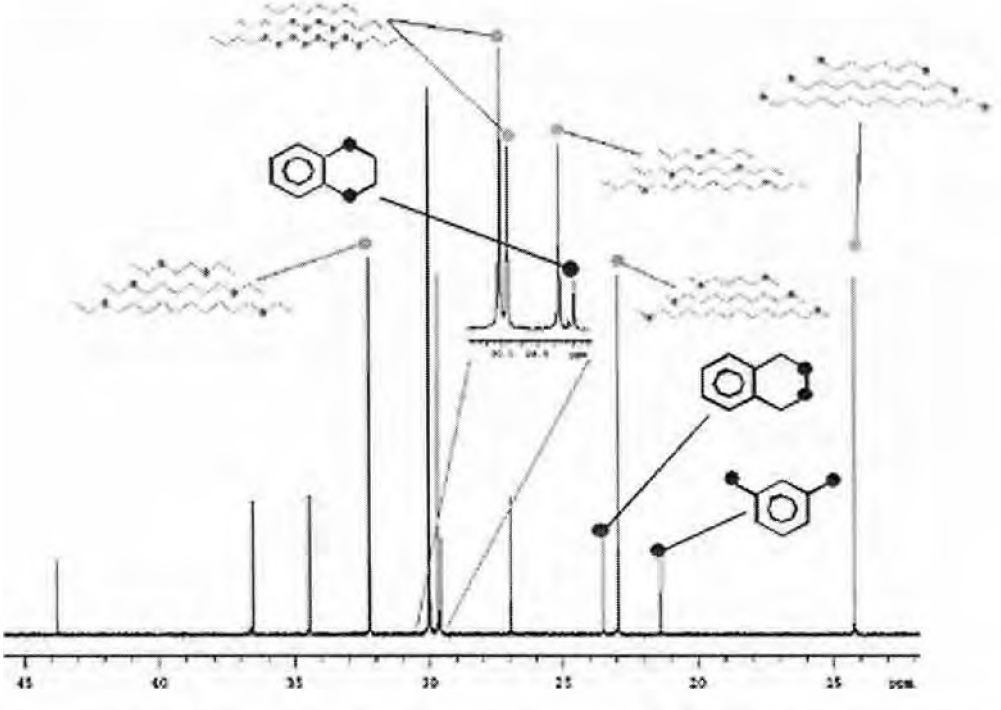


Figure 3. The aliphatic region of the carbon-13 spectrum of the Hex12 surrogate fuel showing the assignment of resonances to carbons in the fuel components.

environments. Interestingly, the C4 carbons break the trend to appear 2.5 ppm upfield from the C3 carbons because of steric congestion or gauche shielding from the C3 carbons. This effect is discussed in detail in reference [11]. The shift of the C5 carbons in normal paraffin's again adopt the downfield trend. For chains of length greater than nine, carbons removed from the chain ends by more than five carbons exhibit shifts differing very little from that of C5, since their bonding environments differ very little from that of C5. Note that attachment to a phenyl ring moves the shift of the alkyl carbons near the attachment point downfield because the phenyl ring has a large electronegativity compared to the alkyl groups, and the phenyl carbons are sp^2 rather than sp^3 hybridized

Chemical shifts of aromatic carbons in surrogate model compounds, i.e., m-xylene and tetralin, are shown in Figure 4. In general, protonated aromatic carbons appear between 120-130 ppm while non-protonated (substituted) aromatics appear downfield from 130-139 ppm. Bridgehead (ring junction) carbons of polynuclear aromatics can also appear upfield from 130 ppm.

There are numerous practical issues associated with obtaining accurate NMR data. These are discussed in many standard NMR texts. Several of particular importance in the context of jet fuels will be briefly mentioned here.

The high precision with which chemical shifts can be measured in jet fuels and surrogates yields a wealth of information about the types of chemical structures contained in any given sample. This high precision can be maintained only with careful attention to magnet shimming and adequate digitization of the NMR signal. Of equal importance, however, is knowledge of the amount of each type of structure present

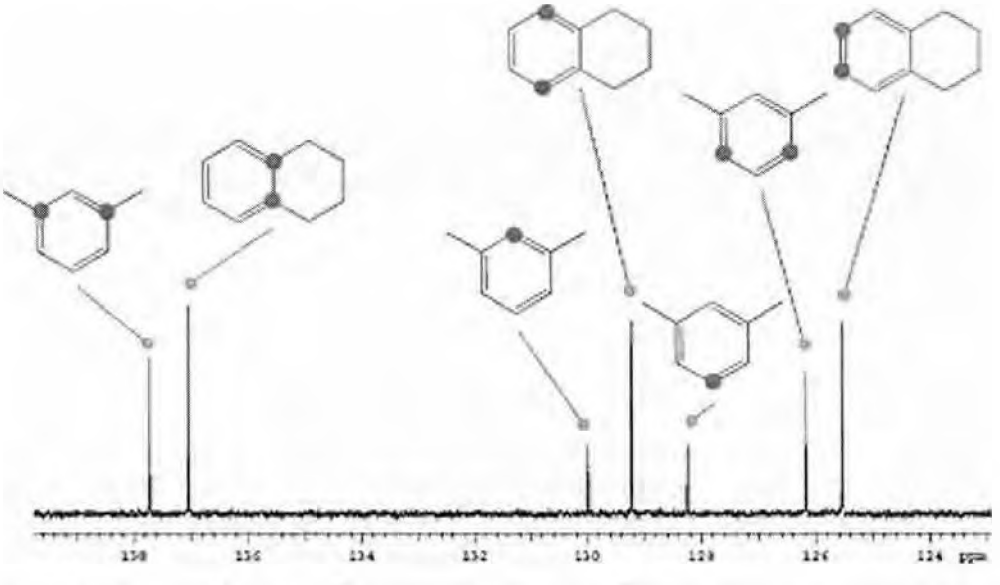


Figure 4. The aromatic region of the carbon-13 spectrum of the Hex12 surrogate fuel showing the assignment of resonances to carbons in the fuel components.

in the material being studied. Obtaining accurate quantitative data from carbon-13 NMR spectra requires that careful attention be paid to several practical issues associated with obtaining the spectra.

The intensity of a carbon resonance is proportional to the number of carbons at thermal equilibrium in the sample that contribute to that particular resonance. However, the proportionality constant is not necessarily the same for all the carbons in a sample due to a combination of the Nuclear Overhauser Effect (NOE) and the thermal equilibrium of the carbon atoms . Thus, the relative intensities of various resonances do not necessarily represent the relative number of carbons contributing to each resonance. The NOE arises from broadband decoupling of protons according to Equation (2),

$$I = (1 + \eta)\, I_0 \tag{2}$$

where I is the observed intensity of the resonance, I_0 is the thermal equilibrium intensity of the resonance with no NOE, and η is the enhancement factor that can take on values between 0 and 1.988. Using gated decoupling, the NOE can be suppressed [11] so that $\eta = 0$, and $I = I_0$. By suppressing the NOE, the intensities of various resonances can be normalized and do represent the relative number of carbons at thermal equilibrium contributing to each resonance. The spectra shown in Figure 3 and Figure 4 were acquired with the NOE suppressed.

The longitudinal relaxation time (T_1) is a measure of the time necessary for the magnetization of a sample to assume its thermal equilibrium value when disturbed from thermal equilibrium. Obtaining an NMR spectrum involves disturbing the sample from thermal equilibrium by means of a radio frequency (rf) pulse and usually requires time averaging by multiple repetitions of the rf pulse . Since different carbons have different T_1's it is necessary to wait five times the longest T_1 before initialing the next rf pulse so that thermal equilibrium can be re-established. Otherwise, the carbons with longer T_1's will exhibit lower intensities relative to those with shorter T_1's resulting in non quantitative results.

The structural details derived from NMR data for the JP-8 modeled in this study are presented in Table 2. The first row provides NMR measurements of the concen-

Table 2. Structure parameters for JP8 and four model jet fuels

	f_a	f_a^H	f_a^N	f_a^S	f_a^B	f_{al}	f_{al}^C	f_{al}^{CH}	f_{al}^{CH2}	f_{al}^{CH3}
JP8	0.11	0.06	0.05			0.89	<0.01	0.16	0.47	0.26
Mod_1	0.109	0.060	0.049	0.035	0.014	0.891	0.004	0.157	0.460	0.270
Mod_2	0.111	0.061	0.05	0.038	0.012	0.889	0	0.160	0.469	0.260
Mod_3	0.112	0.061	0.051	0.038	0.012	0.888	0	0.160	0.463	0.265
Hex12	0.153	0.102	0.051	0.051	0	0.846	0	0.049	0.688	0.109

f_a, fraction of aromatic carbon; f_{al}, fraction of aliphatic carbon; f_a^H, protonated; f_a^N, not protonated; f_a^S, substituted; f_a^B, bridgehead; $f_a + f_a^l = 1$; $f_a^H + f_a^N = f_a$; $f_a^{IC} + f_a^{ICH} + f_a^{ICH2} + f_a^{ICH3} = f_a^l$; $f_a^S + f_a^B = f_a^N$.

tration of different aliphatic and aromatic carbons. The information on aliphatic carbon is the fraction of total carbon that is aliphatic f_{al} and the subfractions f_{al}^{C}, f_{al}^{CH}, f_{al}^{CH2}, and f_{al}^{CH3} that have 0, 1, 2, and 3 (e.g., quaternary, methyne, methylene, and methyl) hydrogen atoms attached to them. For the aromatic carbons, fa represents the fraction of the total carbon that is aromatic and fa^{H}, fa^{N}, fa^{S}, and fa^{B} are the subfractions of the aromatic carbons that are protonated, non- protonated, substituted, and bridgehead (examples of bridgehead carbons are the carbons at the junction of the aromatic rings in compounds such as naphthalene or the inner carbons in pyrene). For the JP fuel the ratio between the aromatic and aliphatic carbons is 11/89. Of the 11% of the carbons that are aromatic, the protonated/non-protonated ratio is 6/5 with the non-protonated carbons consisting of either bridgehead carbons or carbons with substituent attachments. Of the 89% of the total carbons that are aliphatic, only trace amounts are quaternary (non-protonated), and 16%, 47% and 26% of the total carbons are tertiary, secondary and primary aliphatic carbons, respectively. In addition, NMR data indicates that the average length of the n-paraffins is C_{12}. The table also includes the characterizations of three surrogate fuels that come close to matching the NMR characteristics of the J8 and that of Hex 12 to be discussed in Section 4. The following section describes how these relatively simple (compared to the thousands of compounds in real fuels) model fuels were selected.

3. SELECTION OF MODEL REPRESENTATION OF JET FUELS

The interest here is to obtain model representations of jet fuels that capture much of the detail provided by the GC/MS and NMR characterization of fuels with a limited number of compounds. Since the GC/MS and NMR data were obtained on different fuels a jet fuel composition was selected that was close to the average of the composition of the US average for jet fuels (column 2 in Table 1) and the NMR analysis. In the current study, we assume the JP-8 fuel has a composition very close to the US average of aviation fuels surveyed by Edwards [4, 8], which translates into a 23.6 mole % aromatic fraction. However, the 11% aromatic carbon derived from NMR analysis (Table 2) indicates that the aromatic fraction in the current fuel is near 19.1 mole % by assuming: 1) the average carbon number of jet fuel is 11 [4] and, 2) the average number of aromatic carbons in the aromatic species is 6.3 [9] which was obtained by considering the mole percentages and carbon numbers of benzenes, indans/tetralins, and naphthalenes. Therefore, we slightly reduced the aromatic contents from the average suggested by Edwards and increased the normal paraffin content. We assume in this study a composition of 20.6% (by volume) normal paraffins, 37.9% iso-paraffins, 13.6% mono-cyclo, 11.1% di-cyclo, and 1.3% tri-cyclo paraffins, 9.4% benzenes, 5.1% tetralins/indans, and 1% naphthalenes, which corresponds to a 19.4 mol % aromatic content.

The methodology for arriving at the model representation of jet fuels is that they should meet the distribution between chemical classes, the average number of carbons in each class, and, where available, the number of side chain substituents obtained from GC/MS analyses such as those provided by Edwards [4, 8]. The analysis selects possible combinations that satisfy both these constraints and the additional constraints

imposed by the NMR analysis. The NMR data provides constraints, for example, on the number of side chain substitution on aromatics from the fraction of aromatic carbons that are available for substitution and the length and branching of the substituents from balances on primary, secondary, tertiary, and quaternary carbons. The surrogate fuel formulation methodology is presented in Table 3. The details of the analysis are provided in the Appendix leading to the following constraints on the selection of model representations of our JP-8 (Table 4) and suggested surrogate components (Table 5).

Table 3. Fuel structure characterization steps

Chemical Class	Derivation Steps	Rationale
Class avg mol% n-paraffin 18.1 % iso-paraffin 35.1 % 14.1 % 11.8 % 1.3 % 11.5 % 6.6 % 1.4 %		Average carbon number is 12
		Average carbon number is 11.5
		Average carbon number is 11
		Decide the number of substituents using aromatic C/CH functionalities because there are three aromatic chemical class only
		Only iso-paraffin and naphthene fractions contribute to the aliphatic CH functionality; constrained by availability of species chemistry
	Balance check of aliphatic CH_3	Contributions from all chemical classes are known;
	Length of substituents on cyclics	Balance check of aliphatic CH_3

Normal paraffins include species with an average carbon number of C_{12}. Considerable freedom is available in selecting the paraffin mix as long as the mixture satisfies the average carbon number constraint.

Iso-paraffins include, on average, ≈ 5 primary, > 2.5 tertiary and < 0.3 quaternary carbons with an average carbon number of 12. We used an estimated functional distribution for iso-paraffins, which includes 5.2 primary, 3.6 secondary, 3 tertiary and 0.1 quaternary carbons with an equivalent chemical formula of $C_{12}H_{26}$. One likely composition of C_{12} iso-paraffins is given in Table 6. About 12.5% of iso-paraffins have a quaternary carbon. We assume that a candidate species with a quaternary carbon also contributes 6 primary carbons (4 substituents) because the average number of substituents in the narrow distillate cut of Isopar H ($C_{11.6}H_{25.2}$) is 3.2 [6]. Qualified candidates include 2,4,6,6-tetramethyl octane. The other candidates (87.5%) have no qua-

Table 4. Selection criteria and structural functionalities of various surrogates

Chemical Functionality	C #[a]	Mod 1			Mod 2			Mod 3	
		Selection Criteria[b]	mol%	proposed structure	Selection Criteria[b]	mol%	proposed structure	mol%	proposed structure
Fuel	C_{12}	C_{12}		C_{12}	C_{12}	100	C_{12}	100	C_{12}
n-paraffins	C_{12}	C_{12}	18.1	C_{12}	C_{12}	18.9	C_{12}	18.9	C_{12}
iso-paraffins	C_{12}	C_{12}	55.0	C_{12}	C_{12}	55.6	C_{12}	55.6	C_{12}
Primary		≈ 4 C_1		4	≈ 5.2		5.2		5.2
Tertiary		2.5 C_3		3	≈ 3.2		3.2		3.2
Quaternary		0.5 C_4		0.1	≈ 0		0		0
naphthenes	C_{12}	C_{12}		C_{12}	C_{12}		C_{12}		C_{12}
○			11.4			14.5		15.5	
⬡		Methyl	11.8	Methyl	Methyl	12	Methyl	12.6	Methyl
⬡⬡		Dimethyl	1.3	Dimethyl	Dimethyl	1.3	Dimethyl	0	
# of sub		1.5_{ring}		1.5	1.6_{ring}		1.5		1.5
C_n in sub		2.2_{ring}		2.2	3.0_{ring}		3.0		0
⬡	C_{6+}	C_{6+}	11.5	C_{6+}	C_{6+}	13.5	C_{6+}	13.5	C_{6+}
# of sub		2.7		2.7	2.8		2.8		2.8
C_n in sub		2.5_{ring}		2.5	3.2_{ring}		3.2		3.1
⬡⬡	C_{10+}	Methyl C_{10}	5.0	mono- & dimethyl C_{10}	Methyl C_{10}	5.4	mono- & dimethyl C_{10}	5.4	Methyl C_{10}
# of sub (all)		0.2_{ring}		0.2	0.2_{ring}		0.2		0
# of sub (on)		1		1	1		1		1
⬡⬡	C_{10+}	Methyl & Ethyl C_{10}	1.3	Methyl & Ethyl C_{10}	Methyl & Ethyl C_{10}	1.7	Methyl & Ethyl C_{10}	1.7	Methyl & Ethyl C_{10}
# of sub		1.2_{ring}		1.2	1.2_{ring}		1.2		1

[a] references 4 and 10

[b] derived from experimental data, see the text for detailed derivation

[c] 12.5% 2,4,6,6-tetramethyl octane, 75% 3,5,7-trimethyl nonane and 12.5% 2,3,5,7-tetramethyl octane

[d] 75% 3,5,7-trimethyl nonane and 25% 2,3,5,7-tetramethyl octane

[e] estimated value for Jet-A with average 3.25 substituents and carbon number of 11.6 [6]

ternary carbons and will contribute 2.7 tertiary carbons. If only two species are considered, then the set is likely a mixture of 75% trimethyl nonane and 12.5% tetramethyl octane to match the tertiary carbons. Fortunately, the structures of the two generic species also match the values of other carbon functionalities. Qualified candidates include 3,5,7-trimethyl nonane and 2,3,5,7-tetramethyl octane.

Napthenes (cycloparaffins) have an average number of substituents of about 1.5. All substituents except one are methyl, and the average length of the other substituent is

Table 5. Model representations of JP8 fuel. Mod_1 is for a JP fuel with an average carbon number of 11, Mod_2 (and Mod_3) is with an average carbon number of 11.8.

Mod_1 Components	Mol%	Mod_2 Components	Mol%	Mod_3 (Simplified Mod_2) Components	Mol%
Normal-C_{12}	18.1	Normal-C_{12}	15.9	Normal-C_{12}	15.9
Isoparaffins	35.0	Isoparaffins	35.6	Isopar H	35.6
Cyclohexanes	14.4	Cyclohexanes	14.5	Cyclohexanes	15.3
ethyl	(2.1)	pentyl	(0.5)	pentyl	(0)
propyl	(0.5)	hexyl	(0.9)	hexyl	(0)
ethyl methyl	(9.4)	pentyl methyl	(4.6)	pentyl methyl	(0)
propyl methyl	(2.4)	hexyl methyl	(8.5)	hexyl methyl	(15.3)
Methyl Decalin	11.8	Methyl Decalin	12	Methyl Decalin	12.6
Higher Naphthene	1.3	Higher Naphthene	1.3	Higher Naphthene	0
Benzenes	11.5	Benzenes	13.5	Benzenes	13.5
ethyl methyl	(2.9)	propyl methyl	(2.5)	p-isopropyl methyl	(2.8)
propyl methyl	(0.7)	butyl methyl	(0.8)	butyl methyl	(0)
ethyl dimethyl	(6.3)	propyl dimethyl	(7.8)	propyl dimethyl	(9.3)
propyl dimethyl	(1.6)	butyl dimethyl	(2.4)	butyl dimethyl	(1.4)
Tetralins/Indans	6.6	Tetralins/Indans	5.4	Tetralins/Indans	5.4
methyl tetralin	(3.3)	methyl tetralin	(2.7)	methyl tetralin	(5.4)
dimethyl tetralin	(1.6)	dimethyl tetralin	(1.3)	dimethyl tetralin	(0)
methyl indan	(1.6)	methyl indan	(1.3)	methyl indan	(0)
Naphthalenes	1.3	Naphthalenes	1.7	Naphthalenes	1.7
methyl	(0.7)	methyl	(0.9)	methyl	(0.9)
dimethyl	(0.3)	dimethyl	(0.4)	dimethyl	(0)
ethyl	(0.3)	ethyl	(0.4)	ethyl	(0.9)

Table 6. Model Representation of Components in iso-paraffins.

Mole %	Species	Primary	Secondary	Tertiary	Quaternary
12.5%	2,4,6,6-tetramethyl octane	0.7	0.4	0.2	0.1
12.5%	2,3,5,7-tetramethyl octane	0.7	0.2	0.5	0
75%	3,5,7-trimethyl nonane	3.7	3	2.2	0

about 2.2 carbons. The selection criteria for naphthenes include an average number of substituents of approximately 1.5 and the average length of substituents of 2.2 carbons. In order to estimate a distribution among cyclo-paraffins, we assume that multi-ring compounds are di-substituted and decalins are mono-substituted only to reduce the number of degrees of freedom. The mono-substituted decalins are selected also for simplification of the reaction mechanism because there are only simple lumping

models available in the literature for methyl cyclohexane. Mono-substitution will also ease the generation of chemical mechanisms for these species by reducing the number of possible isomers of fused cyclo-paraffins. With these assumptions and a preference of hexagonal species that is evident in the GC/MS data, the distribution of naphthenes can be represented as follows (Scheme 1), in which R is 80% ethyl and 20% propyl.

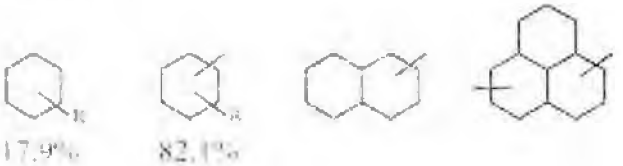
Napthalenes have an average number of substituents of 1.2±0.2. Methyl substitution is dominant. This can be met by a mixture 50% methyl, 25% dimethyl, and 25% ethyl napthalenes

Benzonapthenes have an average number of substituents on the aromatic ring of 1 and on the aliphatic ring of 0.2±0.2. Methyl substitution is dominant. A possible compound distribution that satisfies these constraints is 50% methyl tetralin with the methyl on the benzene ring, 25% dimethyl tetralin with a methyl on each ring, and 25% methyl indan with the methyl on the benzene ring.

Benzenes have 2.7 substituents on average. All substituents excepr one are methyl, and the average length of the other substituent is 2.2 carbons. The estimated values of the number and the length of the substituents on the benzene rings provide two selection criteria to obtain a set of proper surrogate components for the benzene chemical class as shown in the Scheme 2. In the first selection criterion, an average of 2.7 substituents on rings, will divide the generic substituted benzenes Ph-R_x into a substituted toluene (31.3 mol %) and a substituted xylene (68.7 %). In the second selection criterion, with an average of 2.2 carbons per substituent, each candidate sub-class divides into ethyl (80%) and propyl (20%) sub-groups. In reality, the presence of non-, mono- and higher-substituted benzenes, and methyl-only and longer alkyl benzenes cannot be ruled out, but the content of these sub-classes are likely to be small since they are farther removed from the average structures. For the simplicity of the surrogate set, these species are not included in the formulation. The final set of surrogate compounds (Scheme 2) includes 25.0% ethyl toluene, 6.3% propyl toluene, 55.0% ethyl xylene, and 13.7% propyl xylene.

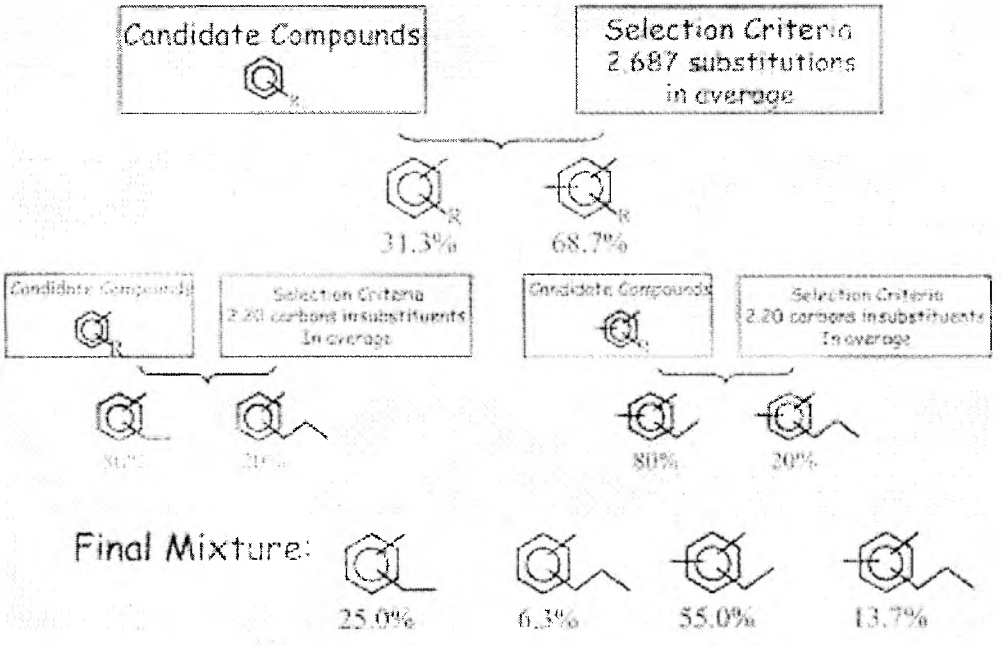
The chemical composition of the model representation of JP-8 derived above (Mod_1) is summarized in Table 5. The carbon functionalities are calculated and summarized in Table 2. The proposed surrogate composition closely matches the NMR experimental data. The structural features of each chemical class are found to compare favorably with the measured values and the selection criteria except the proposed surrogate composition leading to a lower carbon numbers for cyclics (see Table 4). For example, the proposed composition has a $C_{10.1}$ equivalent formula in comparison with C_{12} from the GC /MS data [4, 10].

Scheme 1.



17.9% 82.1%

Scheme 2.



Two additional model representations of JP-8 have been derived. Mod_2, the second column in Tables 4 and 6, adjusts the average carbon number of the JP-8 from a value close to 11 to one closer to 12, to reflect the variability of the reported value of carbon number. Edwards [4] and Duvall et al. [12] reported values corresponding to a chemical formula of $C_{11}H_{21}$ or lower while the data of Hogson and coworkers [10, 13] correspond to an average carbon value of around 11.8, which would correspond to a formula closer to $C_{11.8}H_{22.6}$, using an elemental H/C ratio of 1.9 ± 0.4 based on the Edwards [14] correlation of the US military database on JP-8. Since the carbon length for each chemical class was kept constant, the aromatic content (mol %) for this higher average carbon number needed to be adjusted to 20.6% (in comparison with 26.3% for the US average and 19.4% for Mod_1), so that the aromatic carbon percentage is 11% which is close to that determined by NMR data. Therefore the US average composition for aromatic fractions is reduced proportionally and the reduced percentage is also proportionally distributed to other fractions as shown in Table 5. The proposed surrogate composition (Mod_2) matches the selection criteria very well except for a small deviation of the average carbon number for the benzene fraction. The proposed composition leads to a value of $C_{11.0}$ in comparison with the measured data of $C_{10.7}$ for benzenes and a match of the carbon number of 12 for the napthenes. The third column in Tables 4 and 5 is for a formulation (Mod_3) which takes into consideration the availability of chemicals at reasonable costs. The iso-paraffins are replaced by Isopar H and the napthenes and substituted aromatics, and cyclo-aromatics by compounds that are available at modest cost.

4. SURROGATE FORMULATION USING SOOTING INDEX

The formulations in the above section try to provide mixtures that satisfy both the information on chemical classes, average carbon length, and the carbon types obtained from GC/MS and NMR data in the JP-8 fuels. In principle these should also match combustion behavior. However, the mixtures are complex and are provided to help guide the selection of simpler surrogates, based on considerations of fuel analyses. In the interim, surrogates are selected that match experimental measurements of interest for a specific application. Two illustrations will be provided.

4.1. Surrogates for pool fire simulations

In pool fires the radiation from the soot is of great importance both because it governs the radiation from the flames, the burning rates (determined by the heat flux to the pool and the vapor pressure of the fuel), and smoke emitted by the fires. A surrogate formulation for jet fuels that takes sooting as well as vapor pressure into account is that by Eddings et al. [15]. The mixture was selected to match both the boiling point distribution and the Threshold Sooting Index (TSI). The boiling point distribution of the Jet-A used in the study and that of several surrogates is shown in Figure 5. The surrogate of interest is Hex-12, the composition of which is 3% n-octane, 30% n-dodecane, 12% n-hexadecane, 15% xylenes, 13% tetralin, and 27% decalin. The TSI for Hex-12 was 22.1 compared with 26.7 for the Jet-A. Other physical properties and the heat of combustion of the Jet-A were well matched by the Hex-12 [15]. The success

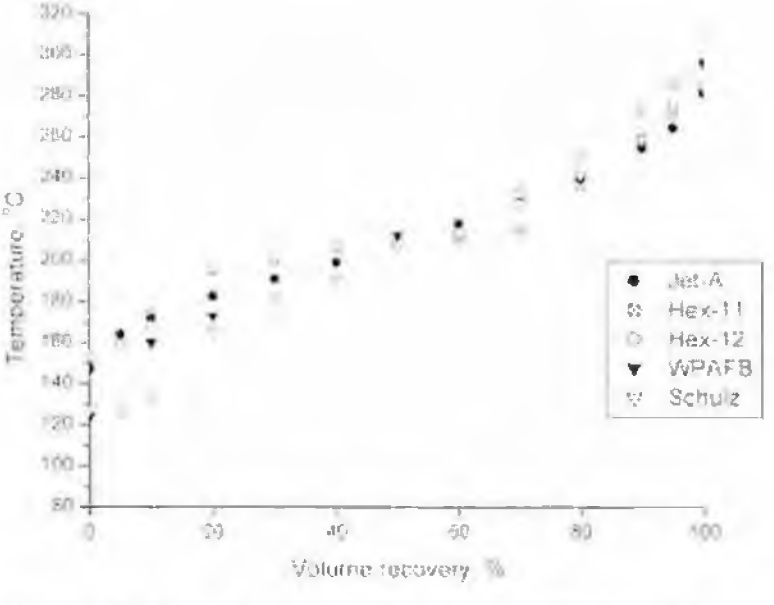


Figure 5. Boiling point distributions for a Jet A fuel and those of various surrogates in the literature.

of the matching of the heat flux and vapor pressure of the Jet-A is determined by the ability of the surrogate to reproduce the rate of burning in a pool fire. Figure 6 provides a comparison of the rate of regression of the burning surface of a 0.3 m diameter pool fire with a pool depth of 0.1 m showing a satisfactory agreement between the regression rates vs. burning time for Jet-A and the Hex-12 surrogate. Analysis of the burning liquid versus time showed that the sooting index for the Jet-A increased with time due to the accumulation of heavier hydrocarbons whereas that of the Hex-12 decreased with time due to the depletion of the relatively light aromatic compounds. If this transient behavior of the soot is to be reproduced then aromatic compounds, which dominate the sooting behavior, should be selected with a range of boiling points to simulate the boiling point distribution of the aromatics in the Jet-A. Despite its ability to match various properties, Hex-12 has quite different carbon functionalities from those obtained from the NMR measurements of the JP-8 fuel as seen in Table 2 as do those of other JP surrogates are described in the literature [1].

4.2. Surrogate for gas turbine combustors

The major priorities in a jet turbine combustor are ignition and blowout, although there are many other considerations [1]. Surrogates for gas turbines are often selected to match experimental data on ignition and extinction. Figures 9 in Colket et al. [1] provide a comparison of the ignition temperature for a fixed fuel mass fraction versus strain rate for a number of surrogates with that of JP fuel. Of the surrogates tested all but two, the

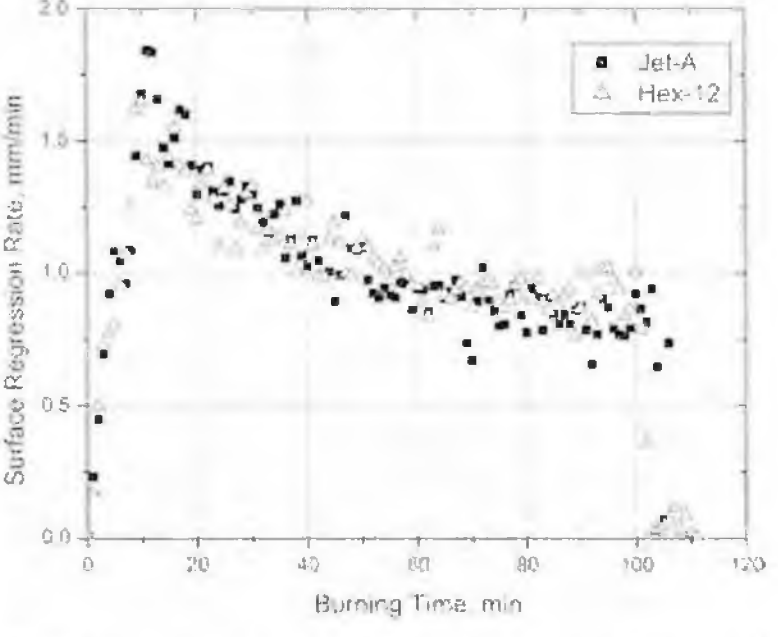


Figure 6. Rate of burning of Jet-A and Hex-12 for a 0.3m diameter pool fire, 0.1m deep.

Aachen surrogates, had a lower ignition temperature at a given strain rate than that for the JP fuel indicating that most of the surrogates were more reactive than the JP fuel. The Aachen surrogates consisted of a mixture of n-decane (or n-dodecane) and 20% by weight 1,2,4-trimethyl benzene. Their ignition temperatures were greater than that of the JP fuel. However the reactivity could clearly be controlled by increasing the amount of TMB, and this provides an attractive two-component surrogate. Similar results were can be seen in Figure 8 of Colket et. al. [1] on a comparison of the fuel/N_2 mass ratio versus strain rate at extinction for a number of surrogates with that of JP fuel. The two-components of an Aachen surrogate are a normal paraffin which has a low sooting tendency and an aromatic compound that has a high sooting tendency. The two-component surrogate can be made to work by using the additional degree of freedom of changing the number, position, length, and branching of the alkyl substituents which have a major influence (*vida infra*) on the sooting tendency of substituted benzenes.

4.3. Use of YSI in place of TSI

The TSI is the standard method of measuring the sooting tendency of fuels by determining the length of the wick that will just soot using a standard ASTM lamp. The sooting tendency of a JP fuel is currently matched by adjusting the surrogate composition to give a TSI that matches that of a JP fuel. This methodology cannot be expected to simulate the sooting index under a wide range of combustion conditions. Wick lamps provide a stop gap measure used while mechanistic models for soot prediction are being developed. The recently developed YSI by McEnally and Pfefferle [16, 17] provides a far superior measure of sooting tendency based on the conversion of a wide range of compounds injected into a diffusion flame in small enough amounts not to perturb the flame (see chapter in this book), although involving a more elaborate experimental set up. YSI results not only provide relative sooting potential for a large number of compounds but also provide mechanistic insights. For example, McEnallly and Pfefferle have provided an understanding of sooting potential from substituted benzenes showing that compounds that form benzyl structures are rate limited by the formation of benzyl radical, that compounds that go quickly to a C_5 second ring have a YSI similar to naphthalene, and compounds that form styrene/phenyl acetylene also are highly sooting. The work of McEnally and Pfefferle is particularly relevant to the multiply substituted benzenes that are prevalent in jet fuels, showing that the 1,2 substituted compounds are highly sooting because of their potential of forming naphthalene. Given the prevalence of substituted benzenes in JP fuels the application of the YSI can be used to modify the sooting propensity of a substituted benzene to be used, for example, in a two-component surrogate such as the Aachen surrogate.

5. PROSPECTS FOR SURROGATE FORMULATION BASED ON KINETIC MODELS

The compositions in Table 4 provide representations of the composition of JP fuels that match the major features (chemical classes, average carbon number, NMR analysis)

of an average JP fuel. In the long run, such compositions could be used to define JP surrogates. In the short term, the composition can be used to define simpler surrogates that match simpler surrogate mixtures that capture the more important aspects of the chemistry of the JP fuel. For example, the compositions in Table 4 could be used to obtain the YSI of a JP fuel in place of having to run an experiment. The YSI could then be used to define the composition of simple, two or three component, mixtures that should provide a good match of the sooting tendency of the real fuel. This presumes the availability of kinetic mechanisms for the components that can predict soot formation. Other chapters in this book describe the progress that has been made in modeling soot formation, usually for simple fuels. This section will provide selected vignettes on the ability of current mechanisms on gas phase kinetics that can be used to predict the trends in soot precursor formation (e.g., benzene and naphthalene) as a function of classes of fuel constituents, of the size and branching of paraffins, and of the side chain substituents for benzene in order to underline those aspects of the details of the chemical composition that are important for soot formation.

The Utah Surrogate Mechanisms developed for modeling composite fuel combustion provides a tool for studying benzene formation in flames based on the structural functionality of the fuel. The mechanism was validated for an atmospheric premixed kerosene flame with an equivalence ratio of 1.7 [18] using a surrogate of five components (n-dodecane, isooctane, methyl cyclohexane, benzene and toluene), and then used to model flames burning each surrogate component under the same experimental conditions. The relative importance in benzene formation of each component in the kerosene surrogate was found, as expected, to follow the trend: aromatics > cycloparaffins > iso-paraffins > normal-paraffins. The fractions of the benzene formation contributed by each component are summarized in Figure 7. Although n-dodecane constitutes approximately three quarters of the fuel used, its contribution to the ben-

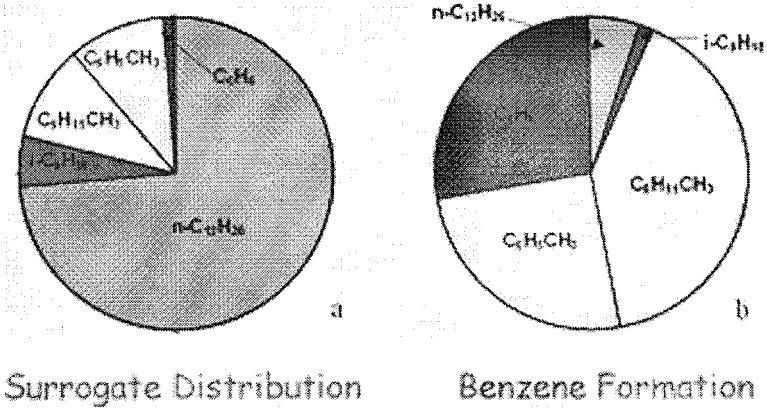


Figure 7. Benzene sources in the kerosene flame (right) from the surrogate components in the fuel (left). Data are re-interpreted from ref 17. The contribution to benzene formation of an individual component is estimated to be the benzene concentration in the modeled flame of that individual component multiplied by its mole fraction in the fuel.

zene formation is minor. The major contributors to benzene formation are methyl cyclohexane and toluene. Cyclohexanes form benzene via dehydrogenation [19, 20], and toluene generates benzene via dealkylation; the entire subject was reviewed recently [21].

The following application of the Utah Surrogate Mechanisms is to demonstrates the impact of changes in size and branching of paraffins on benzene formation for a premixed stoichiometric flame at atmospheric pressure with a European gasoline using a surrogate formulation of 22 compounds that closely approximates the real fuel [22]. Flames were modeled burning individual components at the same experimental conditions. The importance of molecular weight and branching factor on the benzene formation in the gasoline flame is evident in the results in Figure 8. Soot increases with increasing chain length and increased branching, consistent with the experimental results of McEnally and Pfefferle [17].

The third set of simulations, summarized in Figure 9 is related to the role of benzene substituents on the formation of PAHs with two (naphthalenes + indenes) or more rings. The aromatics larger than naphthalene and indene are widely believed to be the major soot precursor species. The formation, shown in Figure 9, of C_{10}+ aromatics increases with carbon number in the order of propyl benzene > ethyl benzene > toluene as well as with increases in the number of substituents on the benzene rings. Xylene produces more aromatics than ethyl benzene, and ethyl toluene produces more than propyl benzene although each pair has a same carbon number. The patterns of the aromatic formation potential summarized from the modeled flames were suppor-

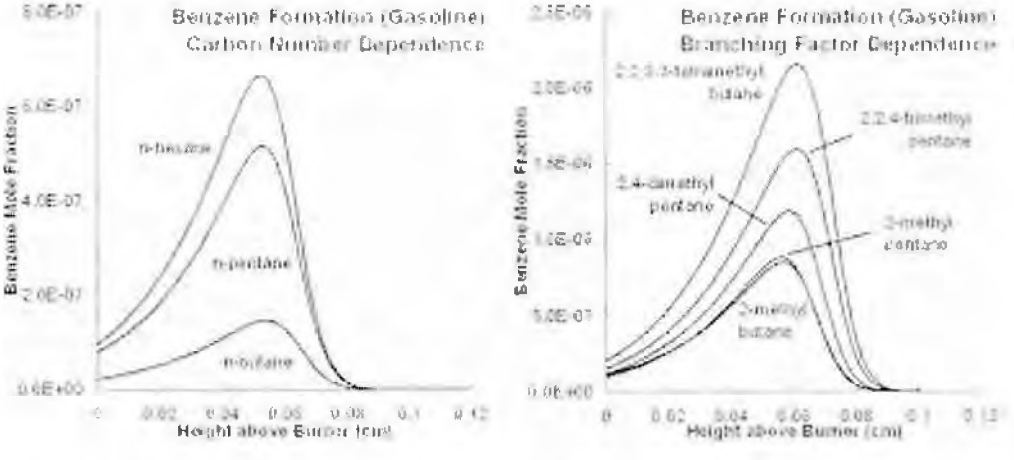


Figure 8. Predicted benzene concentrations in modeled flames burning paraffinic surrogate components (n-butane, n-pentane, n-hexane, 2-methyl butane, 2-methyl pentane, 2,4-dimethyl pentane, 2,2,4-trimethyl pentane, 2,2,3,3-tetramethyl butane) using experimental conditions of a validated atmospheric premixed flame of a European gasoline. The benzene formation potential following the order of carbon number: n-butane < n-pentane < n-hexane and 2-methyl butane < 2-methyl pentane; and the order of branching: 2,4-dimethyl pentane < 2,2,4-trimethyl pentane < 2,2,3,3-tertramethyl butane.

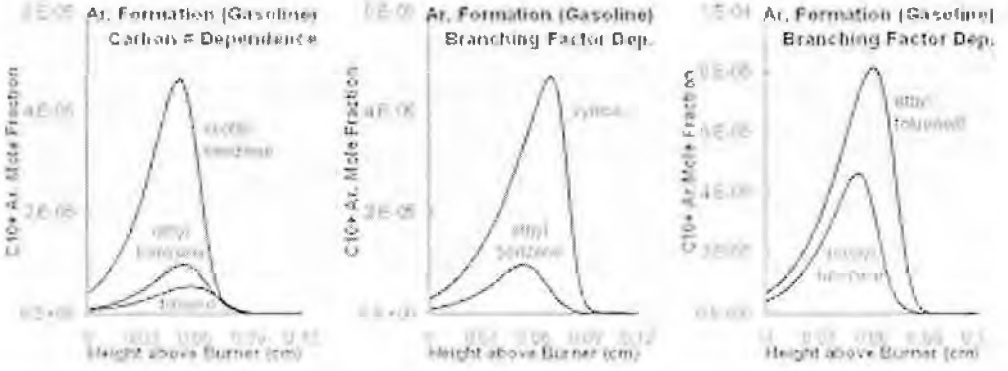


Figure 9. Predicted benzene concentrations in modeled flames burning aromatic surrogate components (toluene, ethyl benzene, xylene, propyl benzene, ethyl toluene) using experimental conditions of a validated atmospheric premixed flame of a European gasoline. The C10+ aromatic formation potential following the order of carbon number: toluene < ethyl benzene < propyl benzene and xylene < ethyl toluene; and the order of branching: ethyl benzene < xylene and propyl benzene < ethyl toluene.

ted by experimental evidence as published by McEnally and Pfefferli [16,17, 23, 24]. The yield sooting indices (YSI) measured in their co-flow methane flame doped with 400 ppm aromatics include toluene (YSI is 43.5) < xylene (*o*, *m*, *p* = 50.0, 53.2, 51.2) < ethyl benzene (53.6) < propyl benzene (55.9) < ethyl toluene (*o*, *m*, *p* = 61.9, 64.0, 60.0). These trends show the problems that exist with the following rules of thumb: "Soot decreases with increases in H/C ratio;" or "Soot increases with increasing fraction of aromatic carbon". Both rules give the inverse trends to the data on which the YSI is based.

6. CONCLUDING COMMENTS

The information provided by NMR and GC/MS data provide a representation of JP fuels that are much more complicated than the current surrogate fuels, particularly those having constituents with a much larger number of side chain substituents than are normally used in surrogate formulations. The substituents on both paraffins and aromatic compounds have been shown by the Yale and Utah researchers [16, 17, 21-23] to increase sooting tendency. The impact of these substituents depends on their structure and ring position and need to be taken into account in formulating JP surrogates that correctly reproduce the sooting potential of the parent fuel, e.g., by matching the YSI. The data on YSI provide a measure of sooting tendency on, among others, the average molecular weight, the branching factor, the number of substituents of cyclo-paraffins and aromatics, the length of substituent chains, and the number of rings. Given the difficulty of matching the composition of JP fuels with affordable components, sensitivity studies, experimental and computational, are needed to determine the extent to which the substituents must be matched. The detailed knowledge

of the structural properties of JP fuels is probably best used to guide the selection of simple mixtures of affordable components rather than serve as a surrogate composition, until kinetic models become available for the more complicated compounds present in real fuels.

ACKNOWLEDGMENTS

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APPENDIX

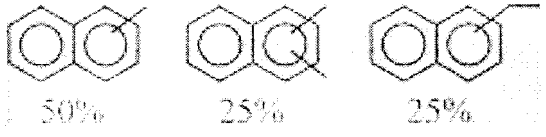
Detailed structural composition, e.g., number of substituents and length of carbon chains, will be derived from NMR spectral data and chemical class distribution information. Some of the structural features are easier to determine than others. For example, the carbon number of the normal paraffin class has been determined in experiments to be 12. The average number of substituent carbons on naphthalenes is 1.5 because the average carbon number for this class is 11.5 and there are 10 carbon atoms in the naphthalene base frame. Because the average carbon number of tetralin/indan is 11, dominant species in this class are mono or di-methyl rings, although the difference between 9-carbon indan and 10-carbon tetralin provides more degrees of freedom in choosing candidate compounds. For each chemical class, the derivation is described in detail here.

The average carbon number of normal paraffinic species is 12 reported by Hodgson and Kemmer [10], which is confirmed in the current study from results of GC-FI-TOFMS. Although most chemical properties depend on carbon number of normal paraffins, it is highly likely that the lower and the higher ends of the normal paraffin compound distribution will compensate each other in terms of average properties. Therefore, a few normal paraffin species averaged at dodecane should be adequate for most applications. In Table 1, the average physical properties of normal undecane, dodecane, and tridecane were used to derive the molar distribution of chemical classes. However, the candidate species for the normal paraffin class are not necessarily limited to a consecutive homologous series. For example, decane, dodecane, and tetradecane could have equally been selected. The inclusion of a wider range of paraffins is especially attractive if matching a continuous spectrum of physical properties is necessary. For example, smaller and larger paraffins might be included in the surrogate to reproduce the boiling range curve that is between 140 C and 280 C, corresponding to C_7 to C_{14} aromatics, C_8 to C_{15} naphthenes, and C_9 to C_{16} paraffins. Considerable freedom is available in choosing candidate species for the normal paraffin class. It is noteworthy that the number of candidate compounds will not alter the average calculated values for carbon atom characterization listed in Table 1 as long as the average carbon number of those compounds is 12.

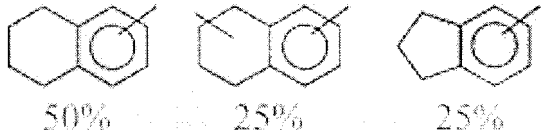
The average carbon number of naphthalenes is 11.5 [10], which indicates the dominant species in the jet fuel are methyl-, dimethyl- and ethyl-naphthalenes. The fraction of naphthalenes higher than C_{13} must be small, because their existence should be balanced by the naphthalene fraction, which accounts for only 0.13 vol % in the world survey of 55 jet fuels, in comparison with 1.55 % for substituted naphthalenes. If the surrogate set includes only methyl-, dimethyl- and ethyl-naphthalenes, it is concluded that 50% of the class is methyl naphthalene, in order to match the average carbon number of 11.5. For a first approximation, dimethyl- and ethyl-naphthalenes are selected with equal importance in this work. Therefore, the selected compounds for the naphthalene class include 50% methyl, 25% dimethyl and 25% ethyl naphthalenes as shown in Scheme 3. The average number of substituents is $50\% \times 1 + 25\% \times 1 + 25\% \times 2 = 1.2$. It is noted that the distribution between dimethyl and ethyl naphthalenes can provide an additional degree of freedom that results in a range of the average number of substituents from 1 to 1.5.

The average carbon number for the indan/tetralin chemical class is 11 [10] and the dominant species have one or two substituents. The evidence of substituents on the aromatic rings is found in the NMR spectrum for the fuel as the peaks at 125.0, 126.2, 129.0 and 129.7 ppm are indicative of the substituent bearing aromatic carbons. It is very difficult to quantify the amount of substituents on the aliphatic ring of benzo-naphthenes since these NMR peaks are superimposed with aliphatic carbons from paraffins. In GC/MS data, substituents on the aromatic ring of benzo-naphthenes were found to be more abundant than those on the aliphatic ring. Therefore, we assumed in this work that mono-substituents of benzo-naphthenes are dominantly on aromatic rings. For di-substituted species, we assume only one substituent on each of the rings. Because there is a very small fraction of non-substituted naphthalenes identified in jet fuels [4], we assume that for the benzo-naphthenes substituted compounds also dominate. Therefore, the inclusion of dimethyl or ethyl tetralins (C_{12}) should be balanced by methyl indan (C_{10}) in order to match the average carbon number of 11. Therefore, a combination, as in Scheme 4, is formulated with a small indan content of 25%. The exclusion of ethyl tetralin is to favor multi-substituted species. The average

Scheme 3.



Scheme 4.



subsituents on the aromatic ring is 1 as seen in Scheme 4. The number on the aliphatic ring is 0.2 and the total number of substituents, on average, is 1.2. A range of the average number of substituents on the aliphatic ring from 0 to 0.5 can be assigned due to the freedom concerning methyl tetralin.

The average carbon number of jet A-type fuels is approximately 11 [4], and NMR data in Table 2 indicates that 5% of the total carbon in the fuel is non-protonated aromatic carbon. Therefore 11 × 5% = 0.5 atoms out of the equivalent chemical formula C_{11} are non-protonated aromatic carbons. The contribution to this carbon functionality from the selected naphthalene surrogate species is (2 + 1.2) × 1.34% = 0.04, and that from the selected benzo-naphthene species is (2 + 1) × 6.58% = 0.2, where 1.2 and 1 are the average numbers of substituents on the aromatic rings selected in this paper for these two classes. Therefore, the contribution from benzenes to the non-protonated aromatic carbons is 0.5 – 0.04 – 0.2 = 0.3, which translates into 0.3/11.50% = 2.7 substituents, on average, for benzenes.

The NMR data in Table 2 indicates that 16% of the total carbon in the fuel is aliphatic methine carbon. Therefore 11 × 16% = 1.8 atoms among the 11 carbons in the equivalent chemical formula C_{11} are methine carbons. Only naphthenes, benzo naphthenes, and iso-paraffins have tertiary carbons. Because only mono- and di-substituted cyclohexane and mono-substituted decalins were identifiable for jet fuels in GC/MS data, we assume the average methine carbon number of naphthenes is less than 2. The contribution from naphthenes to the methine carbon functionality is 14.4% × 2 – 11.8% × (2 + 2) + 1.3% × (4 + 2) = 0.8. The contribution from benzo naphthenes is 0.02. The average number of methine carbons in iso-paraffins is at least (1.8 – 0.8 – 0.03)/35% = 2.8 carbons. Therefore, we estimate the average number of methine carbons in the iso-paraffin chemical class is approximately 3 because the average number of branches is 3.2 in the narrow distillate of Isopar H [6]. Isopar H has an equivalent chemical formula of $C_{11.6}H_{25.2}$, which is the closest isopar cut to the average carbon number (C_{12}) of iso-paraffins in jet fuels [14]. If the average number of branches in iso-paraffins is 3, then the contribution of this class to methine carbons is 35% × 3 = 1, which translates into a contribution of 1.8 – 1 – 0.02= 0.8 methine carbons from naphthenes. The average number of substituents on naphthenes is (0.7 – 11.78% × 2 – 1.28% × 4) / (27.43%) = 1.5, where the 2 ring-fused carbons in decalin and 4 others in multi-ring compounds are accounted for.

The average number of aliphatic quaternary C in iso-paraffinic species is at most 0.3, which corresponds to 1% of the total carbons in the assumed formula $C_{11}H_x$ for JP fuel with the assumption that the iso-paraffin content in the current fuel is 35 vol %, i.e., near the average of US JP-8 fuels.

These estimates provide enough detail to derive the average number of methyl carbons in iso-paraffins. With an average carbon number of Jet-A type fuels of approximately 11 [4]. The NMR data in Table 2 shows 26% of the total carbon in the fuel consists of methyl groups. Therefore 11 × 26% = 2.9 atoms among the 11 carbons in the assumed formula for JP fuel are methyl carbons. The contribution from normal paraffins is 18.12% × 2 = 0.4 atoms; that from naphthenes is (14.37% + 11.78% + 1.28%) × 1.477 = 0.4; that from benzenes is 11.5% × 2.687 = 0.3; that from naphthalenes and benzo naphthenes is (1.34% + 6.58%) × 1.25 = 0.1. Therefore the contribution to this carbon functionality from iso-paraffins is 1.2 methyl carbons of the 11 in the assumed

formula for JP fuel, which corresponding to 1.6845/35.05% = 3.4 methyl carbons per iso-paraffin molecule on average. This value is in the vicinity of the average number of methyl carbons (5.2) in Isopar H.

The length of substituents on the mono-cyclic compounds, i.e., cyclohexanes and benzenes, can be derived by counting the contribution from chemical classes toward the aliphatic methylene carbons. It is noted that we assume methyl-substitution only on naphthalenes, benzo naphthenes, and higher naphthenes. The average carbon number of jet A-type fuels is close to 11 [4], and NMR data in Table 2 indicates that 47% of the total carbon in the fuel is methylene carbon. Therefore 11 × 47% = 5.2 atoms among the 11 carbons in the assumed formula for JP fuel are methylene carbons. The contribution from normal paraffins to this carbon functionality is 18.12% × 10 = 1.8 (Only 10 of the 12 carbons in n-dodecane are methylene). We use the structural details of the narrow distillate cut Isopar H to estimate the functionalities in iso-paraffins. We assume 0.2 methyl substituents out of the 3.2 total substituents are on quaternary carbons, which leads to, on average, 3.0 methine carbons and 0.1 quaternary carbons (constrained to < 0.3 as discussed earlier). Therefore, we assume there are 3.6 methylene carbons on average per iso-paraffin molecule since the average carbon number of iso-paraffins is 12 (Table 1) for jet A-type fuels. The contribution of methylene carbons from iso-paraffins is 1.3; that from the ring portion of naphthenes is 14.37% × 6 + 11.78% × 8 + 1.28% × 10 – (14.37% + 11.78% + 1.28%) × 1.477 = 1.5; that from benzo naphthenes is 0.2. Therefore, the contribution from the substituent chains on the mono-cyclic compounds is about 0.3, which corresponds to 0.3131/(14.37% + 11.50%) = 1.2 secondary carbons. Therefore, the average length of the substituents on benzenes and cyclohexanes is 2.2 carbons.

Our results above are supported by some of the detailed compositions of petroleum, other than proprietary industry data, available in the literature on the fingerprinting of hydrocarbons for purposes of forensics on oil spills or determining the origin of petroleum. Evidence of the biogenic source of petroleum is provided by the detection of isoprenoid alkanes (C_{15}, C_{16}, C_{18}, C_{19}, C_{20}) in a 200 million year old Australian oil [24]. Identification of the alkylated benzenes in Paleozoic petroleum [25] showed an unusual abundance of 1,2,3,4-tetramethyl benzene as well as significant peaks for trimethyl benzenes (1,2,3 and 1,2,4), xylenes; toluene had the largest peak followed by the tetramethyl benzene then benzene.

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